Hydrothermal carbonization (HTC) of marine plastic debris

María E. Iñiguez *, Juan A. Conesa, Andrés Fullana

Chemical Engineering Department. University of Alicante. P.O. Box 99, 03080 Alicante (Spain). Phone: +(34) 96 590 38 67 Fax: +(34) 96 590 38 26

* Corresponding author email: maria.iniguez@ua.es

Abstract

Once removed from the sea, some plastics cannot be recycled or reused. This debris has high calorific value what makes them suitable for using as fuel. For this reason, hydrothermal carbonization of a mixture of plastic materials was carried out using seawater as solvent, to examine the characteristics of the final products obtained and to test the feasibility in converting marine plastic debris to fuel. Results showed that an increase in the temperature of the process reduces the content of the inorganic anions and increases the NCV of the hydrochar. In addition, thermobalance was used to look for differences in the thermal decomposition of the different solid residues, being hydrochar at 300 ºC the most affected material. The content of inorganic compounds in the HTC-liquor increases as the process temperature grows. Amides, alcohols and alkanes were the main organic compounds found in all cases. Gases emissions also increased with temperature.

Keywords: Plastics; HTC; Hydrochar; HTC-liquor; Gases; Seawater.

1. Introduction

Marine debris is defined as any persistent solid material that is manufactured or processed and directly or indirectly, intentionally or unintentionally, disposed of or abandoned into the marine environment or in the lakes [1, 2]. This debris favors the transport of organic and inorganic contaminants in the sea [3-7] and they are harmful to organisms and human health [1, 6, 8-10]. In addition, the presence of this debris generates negative socio-economic consequences [11], since they are not aesthetic, which leads to a significant spending of money in cleaning beaches and coasts, and present a danger to fishing and boats.

Since the development of the plastics industry, plastic products are the most abundant around the globe, hence representing 60-80% of the total marine debris [12]. The main reason why plastics are hazardous to the marine environment is their resistance to degradation, usually estimated between hundreds and thousands of years [13]. During this time, chemical contaminants such as polychlorinated biphenyls (PCBs) and dioxins are released into the sea. Furthermore, plastic items are fragmented into small pieces, becoming plastic micro-particles [14], which are very harmful to marine life [15, 16].

The global annual production of plastics is approximately 280 million tons [17, 18], of which, between 4.8 and 12.7 million tons reaches the sea every year [19]. The most commonly polymers found in the marine environment are polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP) and Nylon [20-22]. They are the most frequently used too.

43 According with the lifecycle of marine debris, the produced plastic discards are
44 accumulated in the beaches and float or are washed to the seabed by water columns,
45 suffering a fragmentation. The fate of the plastic is then its collection (via more
46 encouraging), its decomposition (that will last hundreds of years) or ingestion by marine
47 organisms [23, 24].

48 Some plastics cannot be recycled or reused. For this reason, once removed from the sea,
49 one of the process most commonly used for processing this debris is an incineration
50 process. On the other hand, plastic fractions of marine debris also have been landfilled
51 because for years, they were considered waste product with low value; however, today
52 it is known that this waste has a great value [23]. Marine plastic debris has high
53 calorific value. This feature makes them suitable for using as fuel.

54 These plastics are originally good fuels, but due to contact with sea water, they can
55 contain chlorine and other compounds such as bromine, nitrogen,… which are
56 necessary to eliminate before the combustion process. In this way, a hydrothermal
57 carbonization treatment is the best option to improve the properties of these materials as
58 fuels [25, 26]. In addition, using a process of HTC also has other advantages, since there
59 is greater control over the gases emitted and the working temperatures are relatively
60 low.

61 Hydrothermal carbonization (HTC) is one of the most hopeful thermochemical
62 treatments for producing solid carbon-rich fuel (hydrochar) and high value-added liquid
63 [27-32]. HTC can be operated at low reaction condition as compared with combustion,
64 pyrolysis, and gasification [33]. During HTC process, materials are upgraded in hot
65 compressed water inducing hydrolysis, aromatization, dehydration, recondensation and

66 decarboxylation reactions which, giving rise to the formation of high value added
67 products [34].

68 The final products from HTC are solid hydrochar, liquid fraction and a small amount of
69 gases. Hydrochar can be used for several applications such as fuels, catalyst, carbon
70 sequestration and adsorbents [34-36]. Valuable platform chemicals such as acetic acid,
71 furfural, lactic acid, propionic acid, phenolic compounds, hydroxymethylfurfural,
72 levulinic acid, formic acid and succinic acid are found in the liquid fraction [37-39].
73 Depending on feedstock type, various HTC product characteristics could be obtained
74 from HTC.

75 The quality of hydrochar depends on the composition of process liquor, as product
76 formation and overall reaction can be influenced highly by process water quality [40].
77 Both hydrochar and liquid phase depend heavily on feedstock, residual moisture, quality
78 of feedwater and HTC reaction temperature and reaction time [41-44].

79 In general, water is used as liquid phase in most HTC processes. But in this work, it has
80 been considered the possibility of treating the material directly collected from the sea
81 (for example, in a HTC reactor located in a boat) and use seawater as a liquid phase,
82 which is quite novel, since no study has been found in which marine water is used as
83 liquid phase in a HTC process.

84 On the other hand, there are several studies in which HTC of several materials
85 (especially biomass) are studied. However, the lack of detailed knowledge on HTC of
86 marine plastic debris and the issue of marine plastics treatment after collecting from the
87 sea motivated this study. In this way, hydrothermal carbonization (HTC) of a mixture of
88 plastic materials was carried out to examine the characteristics of the final products
89 obtained and to test the feasibility in converting marine plastic debris to fuel.

2. Materials and methods

2.1. Sample preparation

The carbonization of a mixture of the four most common polymers found in the sea (PE, PP, PET and Nylon), was studied. These samples had been submerged in marine water for more than 2 years. The materials were cut to pieces to form the mixture, being the weight proportion of each plastic the same, i.e., 25 wt. % of each one. Seawater was used as the liquid phase of the process.

2.2. Experimental

HTC was conducted in a laboratory scale using a high-pressure batch reactor with stirring. The parameters controlling the process efficiency are temperature, treatment time and solid/liquid ratio (S/L). For the experimental setup, 50 g of the mixture of plastics and 500 mL of seawater were mixed in a 1 L stainless steel liner (S/L equal to 1:10 g/mL). The mixture was heated up to the desired process temperature by a laboratory oven at approximately 3 $K \cdot min^{-1}$, and once this temperature was reached, the sample was maintained in the reactor for 3 h. Experiments at 200, 250 y 300 ºC were carried out.

Hydrochar and liquid fraction were separated by vacuum filtration through Whatman filter paper of 1.2 mm pore size. The hydrochar was dried at 105ºC for 24 h. Then, it was storaged in a plastic container at room temperature, and the liquid fraction was stored in a plastic dark vessel at 4ºC for further analysis. Gases were collected using Tedlar® bags (Restek, USA).

2.3. Characterization of HTC products

2.3.1. Hydrochar

An elemental analysis was performed to each sample (original mixture and hydrochars obtained at 200 ºC, 250 ºC and 300 ºC), and their carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content were determined using a Perkin-Elmer 2400 (Perkin-Elmer, UK). In all cases, the initial weigh of the sample was 50 mg, and sulfamethazine was employed as internal standard. The humidity of the samples was also measured [45]. In addition, the Net Calorific Value (NCV) was determined using a calorimetric bomb AC-350 Leco Instruments, and the inorganic anions content of each sample was measured by ionic chromatography following EPA methods 5050 and 9056 [46, 47].

2.3.2. Decomposition curves of hydrochar

Thermal stability of samples was analyzed by thermogravimetric analyzer. Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in a mixture nitrogen:oxygen = 4:1 (20% oxygen, simulating air composition) with a total flow rate of 100 $mL \cdot min^{-1}$. The samples were heated in the temperature range from room temperature to 950 ºC, at heating rates of 5, 10 and 20 $ºC \cdot min^{-1}$. For all runs, 4 ± 0.3 mg of sample were used.

2.3.3. HTC-liquor

In order to characterize the liquid fraction after HTC process, the inorganic and organic compounds were analyzed. The inorganic anions content of each sample was measured by ionic chromatography following EPA method 9056 [47] and the organic compounds in the HTC-liquor were determined using chromatography C18 columns (VARIAN Bond Elut C18) and methanol as solvent.

In practice, 10 mL of HTC-liquor samples were first passed through the C18 column. Then, 10 mL of methanol was passed, being each sample collected for subsequent analysis by GC-MS. The analysis of the concentrated extractives was performed in a GC–MS (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA) with a HP-5 MS capillary column (Agilent Technologies, USA) in splitless mode. The SCAN mode ranging from 35 to 450 amu was selected to detect all the possible organic compounds.

2.3.4. Gases and volatile compounds

Gases and volatile compounds were collected in Tedlar® bags (Restek, USA) at the end of the experiments. Carbon dioxide, carbon monoxide, oxygen, nitrogen and hydrogen were analyzed by gas chromatography with thermal conductivity detector (GC-TCD) (Agilent 7820). Light hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A). Other non-condensable products were analyzed using an Agilent 5973N mass spectrometer coupled to an Agilent 6890N gas chromatograph (HRGC-MS) with a capillary DB-624 column, working in the SCAN mode.

3. Results and discussion

3.1. Characterization of solid hydrochar

Fig. 1 shows the original mixture and the mixture (ground sample) after HTC process at 200 ºC, 250 ºC and 300 ºC. After this treatment, the solid obtained is more fragile and easier to grind. Also, the color of the sample is darker as the process temperature increases, which is logical, since the sample is more carbonized.

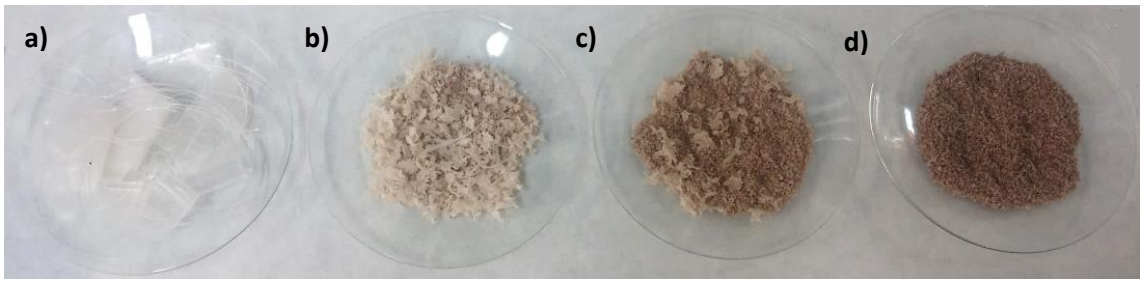


Fig. 1. Original sample and ground sample after HTC process. a) Original mixture; b) 200 ºC; c) 250 ºC; d) 300 ºC.

The results for elemental analysis of the mixture of plastics before and after the hydrothermal carbonization with varying process temperature are illustrated in Table 1. This table also shows the humidity, the ash and inorganic anions content, the Net Calorific Value (NCV) and the yield and the energy yield of each sample.

Analysis shows that an increase in process temperature from 200 ºC to 300ºC increased the carbon content of hydrochar whereas oxygen content decreased. This was reflected by an increase in the NCV from 38.32 to 39.08 MJ/kg. An increase in process temperature also increases the hydrogen content in the solid residue because of side reactions (substitution reaction) [26].

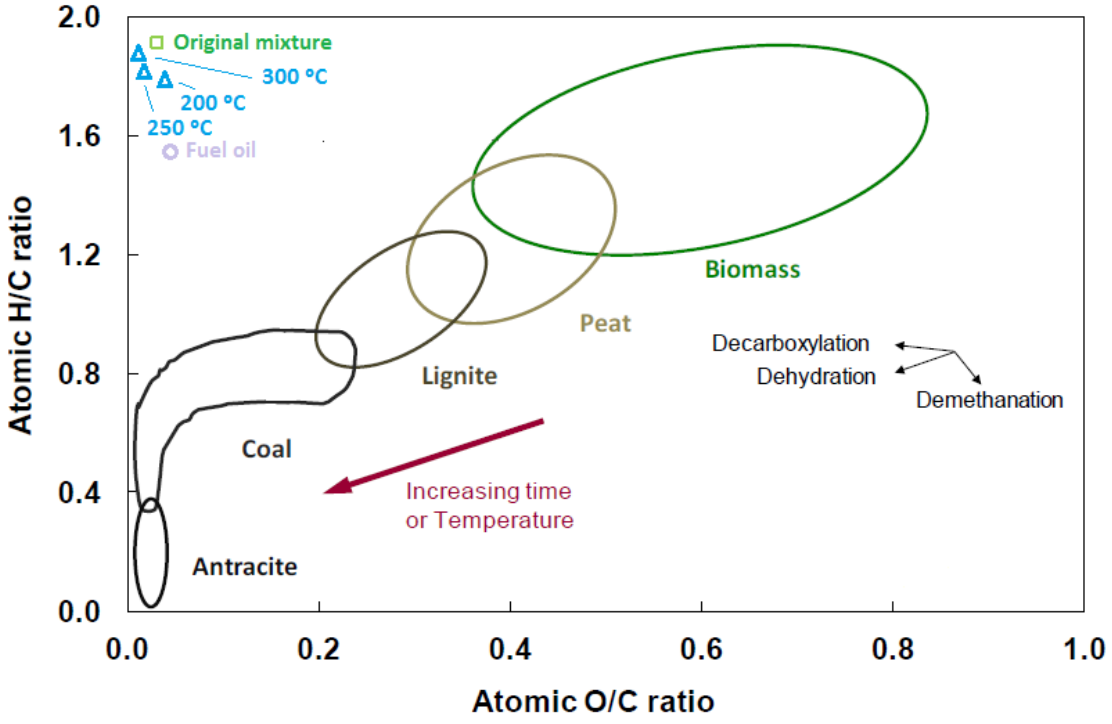
The inorganic anions content was also affected by the process, being the fluorine, chlorine and bromine content lower in the treated material than in the original material. These results are similar to those obtained by other author [26]. In that work, a similar treatment was used to dechlorinate PVC.

176 Table 1. Analysis of the original and HTC solid (wt.% in all cases, except NCV).

	Original	HTC 200 ºC	HTC 250 ºC	HTC 300 ºC
Inmediate analysis				
Moisture	2.00	24.5	22.9	28.7
Ash	5.84	6.95	6.20	5.27
NCV (MJ/kg)	35.6	38.3	38.9	39.1
Yield	-	66.7	40.1	37.4
Energy yield	-	71.8	43.7	41.1
Elemental analysis				
C	77.4	79.0	80.1	80.9
H	12.6	11.9	12.6	13.0
N	2.99	0.60	n.d.	n.d.
S	n.d.	n.d.	n.d.	n.d.
O	1.22	1.45	1.14	0.77
Ionic chromatography				
Fluorine (x 10^{-3})	5.34	2.86	1.53	1.07
Chlorine (x 10^{-1})	4.59	3.17	3.42	4.13
Bromine (x 10^{-4})	11.2	0.97	0.81	0.81

*n.d. = not detected

177 A useful way to describe the fuel characteristics of any solid fuel through elemental
178 concentration is by means of a van-Krevelen diagram. In a typical van-Krevelen
179 diagram, the ratio of atomic hydrogen and carbon is plotted against the ratio of atomic
180 oxygen and carbon, representing the transition from the biomass to anthracite coal. Such
181 diagram is presented in Fig. 2 for the different HTC-hydrochars produced in this study.
182 Fig. 2 shows that in all cases, the ratio H/C to the treated samples falls against to that
183 corresponding to the Original mixture. In addition, the samples are near to the fuel oil,
184 which implies that it is a good fuel.



185

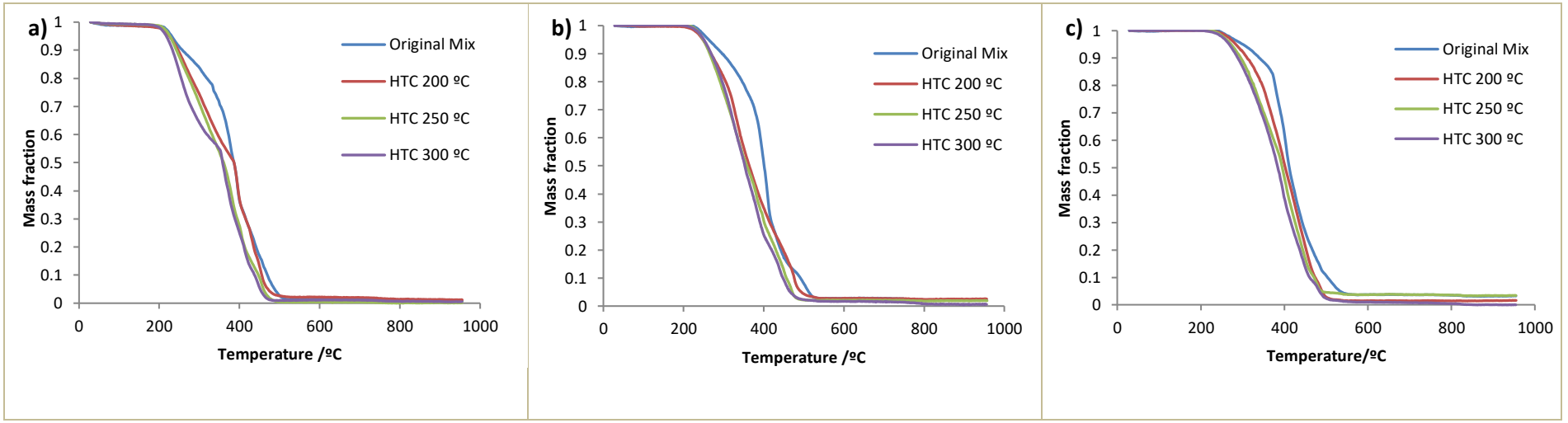
186 Fig. 2. Van Krevelen diagram showing the calification degree achieved in HTC.

187 From these results, it can be concluded that HTC improves the properties of plastic
188 mixture as an energy raw material, since it enhances the carbon content and its heating
189 value.

190 **3.2. Thermal decomposition analysis of hydrochar**

191 Evolution of the thermal behavior of the Original Mix (before HTC process) and the
192 solid residues (after HTC process) was followed by thermogravimetry. Samples were
193 subjected to decomposition in the thermobalance at 5, 10 and 20 $^{o}C \cdot min^{-1}$ and were
194 finally compared. As mentioned before, a mixture nitrogen:oxygen = 4:1 was used as
195 carrier gases to test for the behavior of the samples in combustion conditions. Measures
196 were duplicated to test for the reproducibility that was very good.

197 Fig. 3 shows the decomposition curves obtained for the different solid samples at the
198 different heating rates.



199 Fig. 3. Decomposition curves of hydrochar in combustion conditions. a) 5 ºC·min^{-1}; b) 10 ºC·min^{-1} ; c) 20 ºC·min^{-1}.

Fig. A.1-A.4 (Appendix A) show a comparison of the curves obtained at 5 ºC·min^{-1}, 10 ºC·min^{-1} and 20 ºC·min^{-1} of each material in the atmosphere studied.

As can be seen (Figur. A.1-A.4), when the heating rate increases the mass loss curves moving to the right (higher temperatures). This is an expected behavior taking into account previous works [48-50] in which, a similar behavior was observed for different materials.

Fig. 3 shows important differences in the decomposition of the HTC residues vs. original mix. It is remarkable that the material obtained at 200 ºC already shows significant differences with respect to the original sample, but in general, solid residue obtained at 300ºC presents a greater degradation than the others. In this way, the temperature at which the decomposition rate is maximum decreases in all solid residue obtained after HTC process with respect to the original material, at all heating rates.

3.3. Characterization of HTC process liquid

Table 2 shows the inorganic compounds present at the HTC liquid residue which were analyzed by ionic chromatography. Chloride was the most abundant compound found in the HTC-liquor. Note that PVC was not among the plastics used in the study. Nevertheless, chloride abundance is expected since we used seawater for the process. The content of fluoride, bromide and sulfate increased as the process temperature grows, indicating a possible elimination from the plastic materials. The amounts of the rest of the compounds found decrease with the treatment.

220 Table 2. Inorganic compounds identified in the HTC-liquors generated at 200 ºC, 250
221 ºC and 300 ºC.

	mg/L						
Sample	**Fluoride**	**Chloride**	**Nitrite**	**Bromide**	**Nitrate**	**Phosphate**	**Sulfate**
HTC 200 ºC	0.40	27808	nd	5.72	7.08	7.28	169
HTC 250 ºC	0.48	27035	nd	6.16	6.48	5.96	254
HTC 300 ºC	0.52	24618	nd	9.16	3.96	3.00	241

n.d = not detected

222 To find out all the organic compounds that constituted the liquid phase generated in
223 HTC, HTC-liquor samples obtained at 200 ºC, 250 ºC and 300 ºC were fractionated
224 with methanol, and each fraction was analyzed through GC-MS in SCAN mode. Since a
225 relatively high number of species was expected, which were not even known in
226 advance, detected compounds were only identified using NIST databases (NIST MS
227 Library Version 2.0 d, December 2005). However, no quantification of detected
228 compounds was carried out.

229 Table A.1 (Appendix A) lists the organic compounds identified in the HTC-liquors by
230 GC-MS. It must be remembered that peak areas only allow estimating which would be
231 the major compounds but they are not a direct measurement of the concentration since
232 this depends on the response factor of each substance.

233 Compounds found in the HTC-liquor were grouped by chemical family to estimate the
234 major kind substances. Results, expressed as percentage of total area, are plotted in Fig.
235 4. As can be seen, distribution profiles of the HTC-liquior produced from HTC 200 ºC,
236 HTC 250 ºC and HTC 300 ºC follows different trends. Amides, alcohols and alkanes
237 contribute the most to the total areas, being caprolactam, 4-Methylbenzaldehyde,

benzenesulfonamide, n-butyl- and decane the most noticeable compounds in terms of areas.

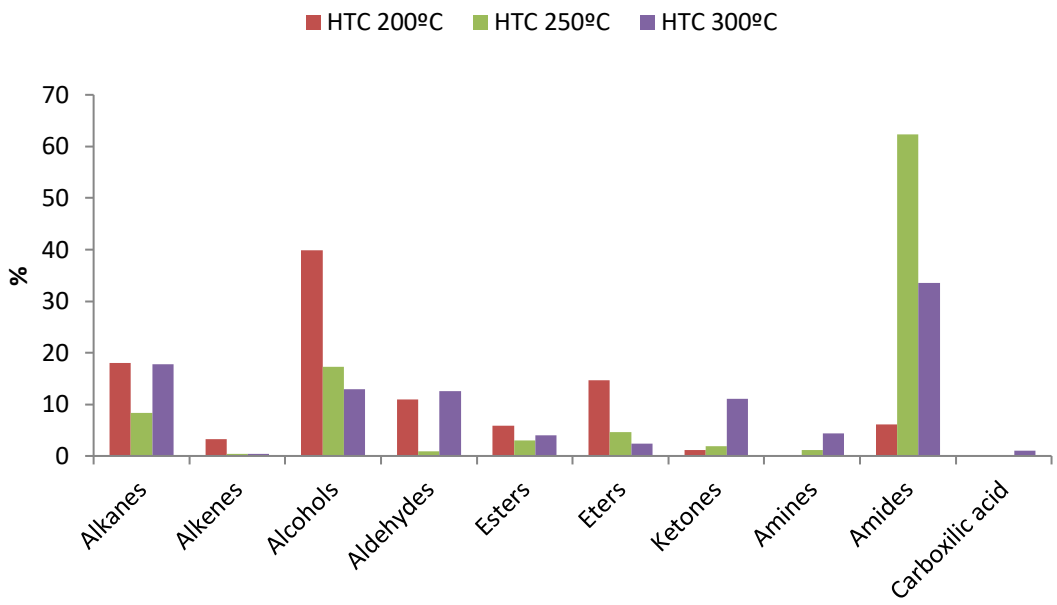


Fig. 4. Distribution profiles of the major chemical groups found in the HTC-liquors produced at 200 ºC, 250ºC and 300 ºC.

In agreement with other work in which the combustion of PE was studied, it is considered that alkanes come mostly from PE [51]. Due to its chemical structure, amides could come mainly from Nylon and probably, alcohols, aldehydes, esters, eters and ketones are generated mostly due to PET.

3.4. Gases and volatile compounds

As mentioned above, HTC of a mixture of plastic was carried out at 200 ºC, 250 ºC and 300 ºC. Table A.2 (Appendix A) shows the yield (mg/kg sample) of the gases emitted during this process. The main gas emitted was nitrogen, presumably from the air filling the reactor before the runs. In all cases, a low value for the emission of carbon monoxide (CO) was observed. However, the production of CO and CO_2 increased with

253 temperature. This may be consequence of the thermal degradation of heavier
254 compounds [52].

255 In agreement with other published work [53] in which combustion experiments of the
256 same plastics were performed, the main light hydrocarbons found were isobutene and
257 methane in all experiments. Additionally, aromatic compounds such as benzene and
258 xylenes were also detected. Moreover, the most abundant non-condensable products
259 detected were acetaldehyde and 2-methyl-1-propene.

260 The yield of the light hydrocarbons and other non-condensable products increased when
261 increasing the temperature from 200 ºC to 300 ºC, which indicate that reactions leading
262 to organic compounds are favored at higher temperatures [54]. On the other hand, a
263 greater number of compounds were generated at 300 ºC.

264 In terms of total emissions of gas, the higher emissions were produced in the treatment
265 at 300 ºC, reaching a value of 822 mg/kg sample (considering high hydrocarbons and
266 other non-condensable products). This value was much higher than those obtained in the
267 processes at 200 ºC and 250 ºC (116 mg/kg sample and 152 mg/kg sample,
268 respectively).

269 To see the evolution of the compounds emitted with the temperature, Fig. 5 has been
270 included. In this Figure, ten of the majority chemical compounds generated during this
271 process have been represented. Thereby, it can see that the emissions of the almost all
272 compounds increased with temperature, being clearly higher in the process at 300 ºC.

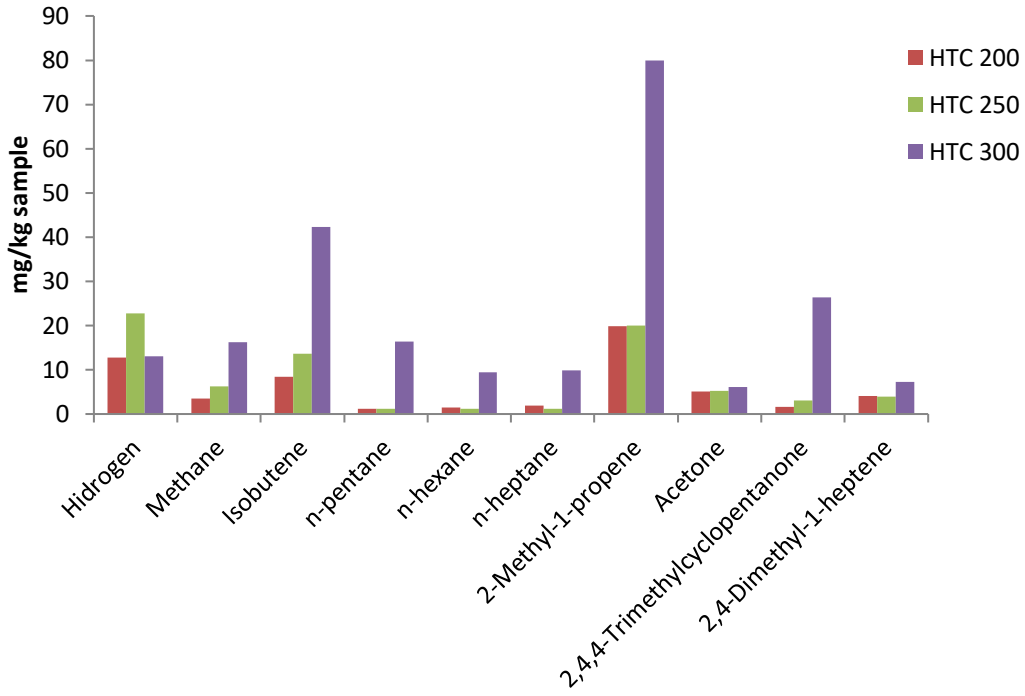


Fig. 5. Distribution profiles of ten of the major chemical compounds found in HTC gases produced at 200 ºC, 250 ºC and 300 ºC.

4. Conclusions

In this work, hydrothermal carbonization (HTC) of a mixture of the four plastics most frequently found in the sea (PE, PP, PET and Nylon) was performed at three different temperatures (200 ºC, 250 ºC and 300 ºC) to examine the characteristics of the final products obtained and to test the feasibility in converting marine plastic debris to fuel.

With respect to the hydrochar, the inorganic anions content in the solid residue was affected by the process, being lower after the treatment. On the other hand, the nitrogen content in the hydrochar also decreases, it is important to avoid the formation of nitrogen oxides (NOx) during the subsequent combustion process. In addition, the NCV increases, reaching a maximum value of 39.08 MJ/kg in the solid at 300 ºC.

Evolution of the thermal behavior of the Original Mix (before HTC process) and the solid residue (after HTC process) was followed by thermogravimetry at different heating rates. The material prepared at 200 ºC shows small differences respect to the original mix, and solid residue obtained at 300ºC presented a greater degradation.

Regarding the HTC liquid residue, chloride was the most abundant compound founds in the HTC-liquor. The content of fluoride, bromide and sulfate increase as the process temperature grows. This is expected since during the HTC, the inorganic anions of the solid material pass into the liquid. On the other hand, the organic compounds were also identified, being amides, alcohols and alkanes the major compounds in all waters. This liquid could be used again in another HTC process.

Additionally, the gases emissions during the process were analyzed. Low emissions of CO were founded and the main gas emitted was nitrogen. Taking into account the high hydrocarbons and other non-condensable products, the higher emissions were detected during the treatment at 300 ºC, reaching a value of 822 mg/kg sample. This gas would not be a problem because it could be subsequently burned.

Taking into account the results, it can be said that from 250 ºC the HTC treatment to this mixture of marine plastic debris would be effective.

More investigations on the HTC of marine debris are required. However, the results show that this process could be a good option to remove plastics to the sea (depending on the degradation they present, most of these plastics cannot be recycled) and use them as fuel, since the solid material obtained has good properties as a combustible and the emissions during the process are low. We would be contributing to improve the environment.

5. Acknowledgements

Support for this work was provided by the CTQ2016-76608-R project from the Ministry of Economy, Industry and Competitiveness (Spain). The author M.E. Iñiguez also thanks the Ministry of Economy, Industry and Competitiveness (Spain) for a Ph.D. grant (contract grant number BES-2014-069473).

6. References

[1] Coe JM, Rogers DE. Marine Debris: Sources, Impacts and Solutions. Springer, New York. 1997.

[2] Galgani F, Fleet D, van Franeker J, Katsanevakis S, Maes T, Mouat J, et al. Marine Strategy Framework directive-Task Group 10 Report marine litter do not cause harm to the coastal and marine environment. Report on the identification of descriptors for the Good Environmental Status of European Seas regarding marine litter under the Marine Strategy Framework Directive. Office for Official Publications of the European Communities; 2010.

[3] Gaylor MO, Harvey E, Hale RC. House crickets can accumulate polybrominated diphenyl ethers (PBDEs) directly from polyurethane foam common in consumer products. Chemosphere 2012;86(5):500-5.

[4] Holmes LA, Turner A, Thompson RC. Adsorption of trace metals to plastic resin pellets in the marine environment. Environmental Pollution 2012;160:42-8.

[5] Mato Y, Isobe T, Takada H, Kanehiro H, Ohtake C, Kaminuma T. Plastic Resin Pellets as a Transport Medium for Toxic Chemicals in the Marine Environment. Environmental Science & Technology 2001;35(2):318-24.

[6] Rochman CM, Hoh E, Hentschel BT, Kaye S. Long-Term Field Measurement of Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris. Environmental Science & Technology 2013;47(3):1646-54.

[7] Teuten EL, Saquing JM, Knappe DRU, Barlaz MA, Jonsson S, Björn A, et al. Transport and release of chemicals from plastics to the environment and to wildlife. Philosophical Transactions of the Royal Society of London B: Biological Sciences 2009;364(1526):2027-45.

[8] Derraik JGB. The pollution of the marine environment by plastic debris: a review. Marine Pollution Bulletin 2002;44(9):842-52.

[9] Gregory MR. Environmental implications of plastic debris in marine settings—entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philosophical Transactions of the Royal Society of London B: Biological Sciences 2009;364(1526):2013-25.

[10] Rochman CM, Manzano C, Hentschel BT, Simonich SLM, Hoh E. Polystyrene Plastic: A Source and Sink for Polycyclic Aromatic Hydrocarbons in the Marine Environment. Environmental Science & Technology 2013;47(24):13976-84.

[11] Mouat J, Lopez Lozano R, Bateson H. Economic impacts of marine litter. Kommunenes Internasjonale Miljøorganisasjon (KIMO International), UK 2010.

[12] Gregory MR, Ryan PG. Pelagic Plastics and Other Seaborne Persistent Synthetic Debris: A Review of Southern Hemisphere Perspectives. In: Coe J, Rogers D, editors. Marine Debris. Springer New York; 1997, p. 49-66.

[13] Barnes DKA, Galgani F, Thompson RC, Barlaz M. Accumulation and fragmentation of plastic debris in global environments. Philosophical Transactions of the Royal Society of London B: Biological Sciences 2009;364(1526):1985-98.

[14] Arthur C, Baker J, Bamford H. Proceedings of the International Research Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris. NOAA Technical Memorandum NOS-OR&R-30 2009.

[15] Andrady AL. Microplastics in the marine environment. Marine Pollution Bulletin 2011;62(8):1596-605.

[16] Cole M, Lindeque P, Halsband C, Galloway TS. Microplastics as contaminants in the marine environment: A review. Marine Pollution Bulletin 2011;62(12):2588-97.

[17] Koelmans AA, Gouin T, Thompson R, Wallace N, Arthur C. Plastics in the marine environment. Environmental Toxicology and Chemistry 2014;33(1):5-10.
[18] Rillig MC. Microplastic in Terrestrial Ecosystems and the Soil? Environmental Science & Technology 2012;46(12):6453-4.
[19] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. Science 2015;347(6223):768-71.
[20] Heo N, Hong S, Han G, Hong S, Lee J, Song Y, et al. Distribution of small plastic debris in cross-section and high strandline on Heungnam beach, South Korea. Ocean Science Journal 2013;48(2):225-33.
[21] Hidalgo-Ruz V, Gutow L, Thompson RC, Thiel M. Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. Environmental Science & Technology 2012;46(6):3060-75.
[22] Martins J, Sobral P. Plastic marine debris on the Portuguese coastline: A matter of size? Marine Pollution Bulletin 2011;62(12):2649-53.
[23] Iñiguez ME, Conesa JA, Fullana A. Marine debris occurrence and treatment: A review. Renewable and Sustainable Energy Reviews 2016;64(Supplement C):394-402.
[24] Cheshire AC, Adler E, Barbière J, Cohen Y, Evans S, Jarayabhand S, et al. UNEP/IOC Guidelines on Survey and Monitoring of Marine Litter. UNEP Regional Seas Reports and Studies, No 186; IOC Technical Series No 83: xii + 120 pp 2009.
[25] Yao Z, Ma X. A new approach to transforming PVC waste into energy via combined hydrothermal carbonization and fast pyrolysis. Energy 2017;141:1156-65.
[26] Lu J, Ma S, Gao J, Freitas Jair CC, Bonagamba Tito J. Study on characterization of pyrolysis and hydrolysis products of poly(vinyl chloride) waste. Journal of Applied Polymer Science 2003;90(12):3252-9.
[27] Coronella CJ, Lynam JG, Reza MT, Uddin MH. Hydrothermal Carbonization of Lignocellulosic Biomass. In: Jin F, editor Application of Hydrothermal Reactions to Biomass Conversion. Berlin, Heidelberg: Springer Berlin Heidelberg; 2014, p. 275-311.
[28] Lynam JG, Reza MT, Yan W, Vásquez VR, Coronella CJ. Hydrothermal carbonization of various lignocellulosic biomass. Biomass Conversion and Biorefinery 2015;5(2):173-81.
[29] Reza MT, Becker W, Sachsenheimer K, Mumme J. Hydrothermal carbonization (HTC): Near infrared spectroscopy and partial least-squares regression for determination of selective components in HTC solid and liquid products derived from maize silage. Bioresource Technology 2014;161:91-101.
[30] Toufiq Reza M, Borrego AG, Wirth B. Optical texture of hydrochar from maize silage and maize silage digestate. International Journal of Coal Geology 2014;134-135:74-9.
[31] Reza MT, Lynam JG, Uddin MH, Coronella CJ. Hydrothermal carbonization: Fate of inorganics. Biomass and Bioenergy 2013;49:86-94.
[32] Reza MT, Lynam Joan G, Vasquez Victor R, Coronella Charles J. Pelletization of biochar from hydrothermally carbonized wood. Environmental Progress & Sustainable Energy 2012;31(2):225-34.
[33] Kalderis D, Kotti M, Méndez A, Gascó G. Characterization of hydrochars produced by hydrothermal carbonization of rice husk. 2014.
[34] Funke A, Ziegler F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. Biofuels, Bioproducts and Biorefining 2010;4(2):160-77.
[35] Bobleter O. Hydrothermal Degradation of Polymers Derived from Plants. Progress in Polymer Science 1994;19:797-841.
[36] Kambo HS, Dutta A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable and Sustainable Energy Reviews 2015;45:359-78.

[37] Becker R, Dorgerloh U, Paulke E, Mumme J, Nehls I. Hydrothermal Carbonization of Biomass: Major Organic Components of the Aqueous Phase. Chemical Engineering & Technology 2014;37(3):511-8.
[38] Xiao L-P, Shi Z-J, Xu F, Sun R-C. Hydrothermal carbonization of lignocellulosic biomass. Bioresource Technology 2012;118:619-23.
[39] Zhu Z, Liu Z, Zhang Y, Li B, Lu H, Duan N, et al. Recovery of reducing sugars and volatile fatty acids from cornstalk at different hydrothermal treatment severity. Bioresource Technology 2016;199:220-7.
[40] Reza MT, Rottler E, Herklotz L, Wirth B. Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide. Bioresource Technology 2015;182:336-44.
[41] Lu X, Berge ND. Influence of feedstock chemical composition on product formation and characteristics derived from the hydrothermal carbonization of mixed feedstocks. Bioresource Technology 2014;166:120-31.
[42] Lu X, Flora JRV, Berge ND. Influence of process water quality on hydrothermal carbonization of cellulose. Bioresource Technology 2014;154:229-39.
[43] Lu X, Pellechia PJ, Flora JRV, Berge ND. Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose. Bioresource Technology 2013;138:180-90.
[44] Reza MT, Andert J, Wirth B, Busch D, Pielert J, Lynam Joan G, et al. Hydrothermal Carbonization of Biomass for Energy and Crop Production. *Applied Bioenergy.* 1. 2014.
[45] UNE-EN ISO. Solid biofuels - Determination of moisture content - Oven dry method - Part 1: Total moisture - Reference method (ISO 18134-1:2015). *18134-1:2016.* Spain: AENOR; 2016.
[46] US EPA. Method 5050. Bomb preparation method for solid waste. In: EPA U, ed. *SW-846.*; 1994a.
[47] US EPA. Method 9056A. Determination of inorganic anions by ion chromatography. In: US EPA, ed. *SW-846. United States Environmental Protection Agency, Office of Solid Waste, Washington, D.C.*; 2000.
[48] Caballero JA, Conesa JA. Mathematical considerations for nonisothermal kinetics in thermal decomposition. Journal of Analytical and Applied Pyrolysis 2005;73(1):85-100.
[49] Conesa JA, Rey L. Thermogravimetric and kinetic analysis of the decomposition of solid recovered fuel from municipal solid waste. Journal of Thermal Analysis and Calorimetry 2015;120(2):1233-40.
[50] Conesa JA, Soler A. Decomposition kinetics of materials combining biomass and electronic waste. Journal of Thermal Analysis and Calorimetry 2017;128(1):225-33.
[51] Aracil I, Font R, Conesa JA. Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride. Journal of Analytical and Applied Pyrolysis 2005;74(1):465-78.
[52] Paabo M, Levin Barbara C. A review of the literature on the gaseous products and toxicity generated from the pyrolysis and combustion of rigid polyurethane foams. Fire and Materials 1987;11(1):1-29.
[53] Iñiguez ME, Conesa JA, Soler A. Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials. Marine Pollution Bulletin 2018;130:249-57.
[54] Atal A, Levendis YA, Carlson J, Dunayevskiy Y, Vouros P. On the survivability and pyrosynthesis of PAH during combustion of pulverized coal and tire crumb. Combustion and Flame 1997;110(4):462-78.